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USING OZONE TO TREAT WELL WATER CONTAINING PESTICIDES
(U) NAVAL OCEAN SYSTEMS CENTER SAN DIEGO CA J P HURLEY
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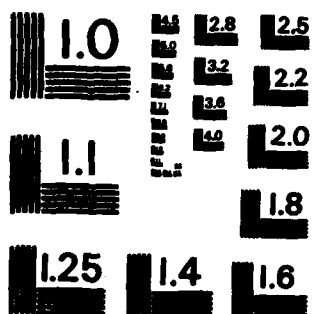


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**USING OZONE TO TREAT WELL
WATER CONTAINING PESTICIDES**

J. P. Hurley
Radiation Physics Branch

July 1984
Final Report

Prepared for
Navy Science Assistance Program
Code 1802

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NAVAL OCEAN SYSTEMS CENTER SAN DIEGO, CA 92152

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

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INTRODUCTION

Traces of 1, 2-Dibromo-3-Chloropropane (DBCP) have been found in the Navy Public Works Center, Pearl Harbor, Hawaii well water (reference 1). At present the well is pumping 8-million gallons per day (mgd) and the DBCP level is less than 20 parts per trillion (ppt). However, the normal pumping rate is 17 mgd and, at that production level, there is concern that the DBCP concentration may increase. It is reported that one recent sample was measured to be 27 ppt (reference 2). As long as DBCP is measurably present in the water, the Navy faces the possibility that the water may be declared unfit for drinking, especially since there are indications that the State of Hawaii may impose an upper limit of 20 ppt on the DBCP contaminant.

Because of the Navy's need to treat the water (there are no alternate sources), and because a literature review revealed no work done specifically on DBCP, it was suggested that ozone, a powerful oxidant and widely used water disinfectant, be tested for effectiveness against DBCP. At the same time it was suggested (reference 3) that ozone also be tested against 1, 2-Dibromoethane (ethylenedibromide, EDB) and 1,2,3-Trichloropropane (TCP), since these are now appearing generally in concentrations high enough to cause concern. Direct queries to the Environmental Protection Agency Laboratory in Cincinnati and the San Diego County Office of Water Quality indicated that neither was aware of any previous test using ozone against these pesticides.

This report will describe the tests made on the subject chemicals and the results of those tests.



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APPARATUS AND PROCEDURES

In the present experiment ozone and oxygen were bubbled through samples prepared by dissolving carefully measured amounts of each of the three pesticides in deionized water. The measurements were preliminary in that gas chromatography was used only to look for reductions, if any, in the initial pesticide concentrations. If the results were to show significant changes in any of the chemicals, then further work using mass spectroscopy to quantitatively identify the organic reaction product would be justified.

At the recommendation of the San Diego County Office of Water Quality, Quality Assurance Laboratory of San Diego was engaged to perform the measurements with the author. Three samples of 100 ml each were prepared by adding DBCP at 50 ppb, EDB at 100 ppb, and TCP at 400 ppb to deionized water. Two of these were subsequently subjected to aeration, one with oxygen and the other with ozone, while the third was used as the initial concentration standard. After aeration, a 10 ml aliquot was taken from each sample to prepare them for gas chromatography. After adding 2 ml of pesticide-quality hexane as the organic solvent and mixing vigorously, the phases were allowed to separate. A 2 μ l sample was then drawn from the organic phase for injection into the chromatograph.

The chromatograph used for these measurements is a Hewlett-Packard Model 5713. The capillary column is 30 m long, 0.25 mm in inside diameter, and has an SE 34 packing. The detector is electron capture and the carrier gas was nitrogen. The temperature cycle began at 80 C for 4 minutes and increased at 16 C/minute, ending at 250 C for 4 minutes.

The ozone generator used to produce the aeration gases is a Sandhill Scientific Model IT which uses a 60 Hz corona discharge between coaxial electrodes to produce ozone. With the flowrate adjusted to 1 ft³/hr (7.9 ml/s), and dry oxygen used as the feed gas, the ozone production was 0.86 g/h. The unit had been calibrated previously by iodometric titration, as described in Standard Methods (reference 4). The samples bubbled vigorously, at the flowrates used for these tests (7.9ml/s), indicating effective contacting (mixing) for the gases in the solutions.

To ensure that the aerations were equivalent for both ozone and oxygen, no changes in either the flowrate or the feed gas were made between aerations. It was necessary only to de-energize the generator electrical circuit to change from ozone to oxygen.

RESULTS AND CONCLUSIONS

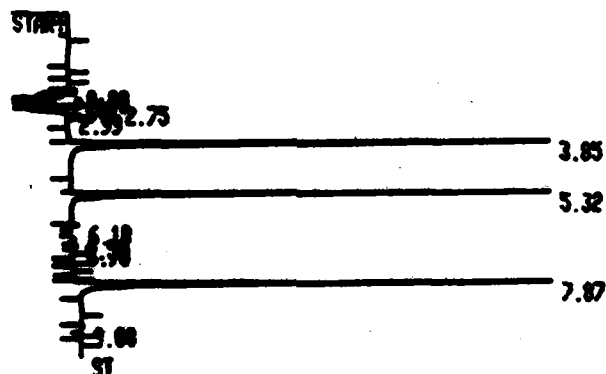
The results of the measurements are shown in the spectra of figures 1, 2, and 3 and are summarized in the Quality Assurance Laboratory report. In each figure the peak at 3.86 retention time (RT) is for EDB at 100 ppb initially; the peak at 5.32 RT is for 1,2,3-TCP at 400 ppb; and the peak at 7.87 RT is for DBCP at 50 ppb.

In figure 1 the chromatograph for the initial (nonaerated) sample is shown. Note that the measured values closely reproduce the initially prepared concentrations. Figure 2 shows the results of the aeration with oxygen. Note that all three organics are reduced; 22 percent, 72 percent, and 44 percent for DBCP, EDB, and TCP, respectively. Figure 3 shows the results of the ozone aeration. Note that they are significantly the same as those for oxygen; 27 percent, 72 percent and 46 percent for DBCP, EDB, and TCP, respectively. These results are summarized again in the QAL report.

It is clear that: 1) for the pesticides tested the reductions in concentrations were due to mechanical purging by the bubbling action of the two gases, and 2) the ozone was not significantly more effective than was the oxygen. The conclusion is that ozone is not an effective agent against these pesticides and it is inadvisable to continue the work.

STANDARD

- 1) EDB
- 2) 1,2,3-TCP
- 3) DBCP



RUN # 273

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BOTTLE # 04

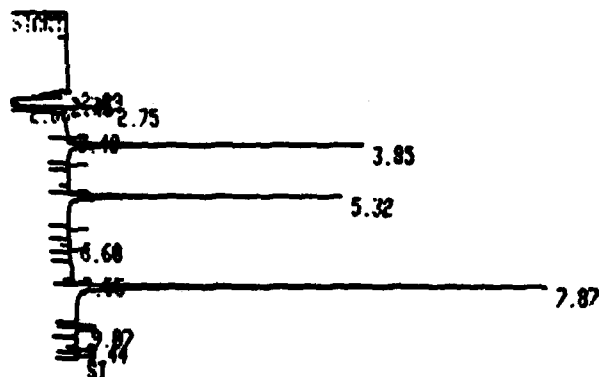
ESTD	RT	AREA	TYPE	CALC	AMOUNT
	3.85	373930	PB	1R	101.100
	5.32	106010	PB	2	410.870
	7.87	276320	PB	3	51.087

TOTAL AREA= 838450
NUL FACTOR= 1.0000E+00

Figure 1. Chromatograph of the standard (nonaerated) sample.

OXYGEN

- 1) EDB
- 2) 1,2,3-TCP
- 3) DBCP



RUN # 274

DEC/21/83 11:59:15
BOTTLE # 06

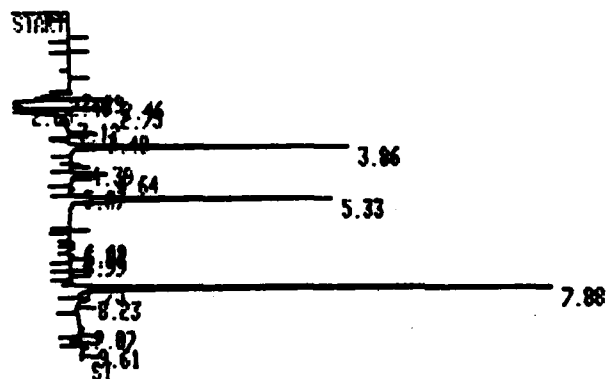
ESTD	RT	AREA	TYPE	CALC	AMOUNT
	3.85	103620	PB	1R	27.867
	5.32	104860	PB	2	231.610
	7.87	214500	PB	3	39.629

TOTAL AREA= 422980
MUL FACTOR= 1.0000E+00

Figure 2. Chromatograph of the sample aerated for 15 minutes with oxygen.

OZONE

- 1) EDB
- 2) 1,2,3-TCP
- 3) DBCP



RUN # 275

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BOTTLE # 07

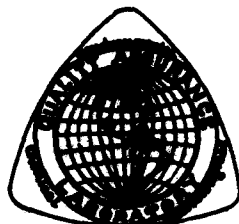
ESTD

RT	AREA	TYPE	CALC	AMOUNT
3.86	102400	PB	1R	27.539
5.33	101030	PB	2	223.150
7.88	200330	PB	3	37.012

TOTAL AREA= 403760
MUL FACTOR= 1.0000E+00

Figure 3. Chromatograph of the sample aerated for 15 minutes with ozone.

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QUALITY ASSURANCE LABORATORY

December 23, 1983


Contracting Officer
Naval Ocean Systems Center
271 Catalina Blvd.
Bldg. A33
San Diego, CA 92152

Date of Sample:
Analyst:
Q.A. Log #:

December 21, 1983
MS
5702-83

The following report concerns a water sample prepared in the laboratory to contain 1,2-Dibromo-3-Chloropropane (50ppb), 1,2-Dibromoethane (100ppb) and 1,2,3-Trichloropropane (400ppb). Two 100 ml aliquots of this sample were subjected to aeration for approximately 15 minutes, one with oxygen, the other with ozone. These samples were subsequently analyzed, the results of which are presented below.

	<u>Fresh Sample</u> (no aeration)	<u>Oxygen</u> (15 min)	<u>Ozone</u> (15 min)
1,2-Dibromo-3-Chloropropane	51 ppb	40 ppb	37 ppb
1,2-Dibromoethane	101	28	28
1,2,3-Trichloropropane	411	231	223


Peter T.L. Shen
Laboratory Director

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2. Mickus, A., NSAPCPF, Private Communication.
3. Boyle, J.M., NSAPNOSC, Private Communication.
4. Standard Methods for the Examination of Water and Wastewater, 1980, American Public Health Association, Washington, DC, pp 399.

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